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## Cohenite as a pressure indicator in iron meteorites ?

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**Abstract**—To evaluate the usefulness of cohenite as a pressure indicator in iron meteorites, the thermodynamics and kinetics of its decomposition have been re-examined. Laboratory experiments on the decomposition of  $\text{Fe}_3\text{C}$  at high pressures (LIPSCHUTZ and ANDERS, 1961b) failed to show the stabilization predicted by RINGWOOD (1960), and it has therefore been necessary to revise the high-pressure portion of the Fe-C diagram. The stability field of  $\text{Fe}_3\text{C}$  becomes greatly constricted, and the stabilisation of cohenite by high pressures no longer seems feasible. If iron meteorites had cooled slowly at pressures of 30–60 kb, (RINGWOOD and KAUFMAN, 1962), cohenite should have decomposed in a matter of hours to graphite or diamond, at temperatures below 640–565°C. The times actually available for decomposition were longer by factors of  $10^{10}$ – $10^{11}$ , and the survival of cohenite therefore seems to require the assumption that nucleation was inhibited by a factor of this order.

If the iron meteorites had originated at low pressures, precisely the same assumption (nucleation inhibited by a factor of  $10^{10}$ – $10^{11}$ ) must be made. Hence there is no longer any reason to attribute the survival of cohenite to high pressures.

Laboratory experiments show that the decomposition of cementite at 680° and 1 atm can indeed be inhibited by factors  $>10^5$ . It does not seem unreasonable that meteoritic cohenite, having a much higher degree of crystal perfection, should be inhibited in its decomposition to an even greater extent.

RINGWOOD (1960) has proposed that the presence of cohenite  $[(\text{Fe,Ni})_3\text{C}]$  in iron meteorites implies high pressures in the meteorite parent bodies. Briefly, his argument runs as follows:

1. The compound  $\text{Fe}_3\text{C}$  is thermodynamically unstable at low pressures, the standard free energy for its decomposition to metallic iron and graphite being  $-4.8$  kcal/mol at 298°K and 1 atm and remaining negative at higher temperatures as well.
2. In the laboratory, cementite† decomposes rapidly in the temperature range 800–1000°C. If, as RINGWOOD assumes, cohenite was already present when the meteorites cooled through this range, it should have decomposed.

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† We shall use the terms "cementite" for the pure compound  $\text{Fe}_3\text{C}$ , and "cohenite" for the meteoritic mineral  $(\text{Fe,Ni})_3\text{C}$ , containing about 2 per cent Ni.

3. The survival of cohenite, paradoxical in view of its thermodynamic and kinetic instability, can be understood if the meteorites had cooled at pressures of 30 kb or greater. At these pressures, the negative free energy of the above reaction is more than compensated by the positive  $P\Delta V$  term.

As an alternative to the high-pressure hypothesis, we suggested that cohenite might have been stabilised by its phosphorus content (LIPSCHUTZ and ANDERS, 1961a). However, RINGWOOD and SEABROOK (1962) found that the phosphorus content (0.10–0.49 wt.%) was too low for such stabilisation. They also noted that individual cohenite crystals heated to 750–950°C decompose in a matter of hours, and suggested that this evidence supported RINGWOOD's earlier conclusion.

Although we are impressed by RINGWOOD and SEABROOK's evidence that the phosphorus content of cohenite is too low to stabilise it to a significant extent, we find ourselves unable to accept their conclusion—that it was stabilised by high pressure. In this paper, we shall treat the problem in a more quantitative manner, and emphasise certain factors that have not received sufficient attention in previous papers on the subject.

Three questions, in particular, must be re-examined as follows:

1. The temperature at which cohenite first appeared in iron meteorites;
2. The thermodynamics of cohenite decomposition, and the stability field of cohenite;
3. The kinetics of cohenite decomposition.

#### 1. FORMATION TEMPERATURE OF COHENITE

Cohenite apparently formed by exsolution from the solid state, during slow cooling of the iron meteorites. To discuss its survival in quantitative terms, one must know the temperature at which it first appeared.

Let us first consider the formation of cohenite in terms of the binary Fe–C phase diagram (Fig. 1), and then make the necessary allowances for the ternary Fe–Ni–C system. Even cohenite-rich iron meteorites generally have carbon contents no higher than 0.4–0.6 weight per cent, that is, less than the  $\alpha$ – $\gamma$  eutectoid composition (0.80 per cent). Only the left-hand portion of the diagram (to the left of point *S*) is therefore relevant. For structural reasons, carbon is much more readily soluble in face-centered cubic  $\gamma$ -phase than in body-centered  $\alpha$ -phase. Hence a hypoeutectoid iron–carbon alloy of the carbon content of Canyon Diablo (0.6 wt.%; BRETNALL and AXON, 1962) cooling from high temperatures remains homogeneous  $\gamma$ -phase down to about 750°C; then, carbon-poor  $\alpha$ -phase begins to precipitate, and the residual  $\gamma$ -phase becomes progressively richer in carbon until the eutectoid temperature (723°C) has been reached. At this point, the alloy breaks down into  $\alpha$ -phase and metastable cementite. Although graphite is the stable reaction product, metastable cementite is favored on kinetic grounds. Thus the steel industry is able to produce cementite in multi-megaton quantities annually.

In the presence of nickel, the situation changes slightly (Fig. 2). Nickel stabilises the  $\gamma$ -phase, causing the  $\gamma$ -field in Fig. 1 to extend to lower temperatures and perhaps to higher carbon contents. On cooling, the carbon again remains in

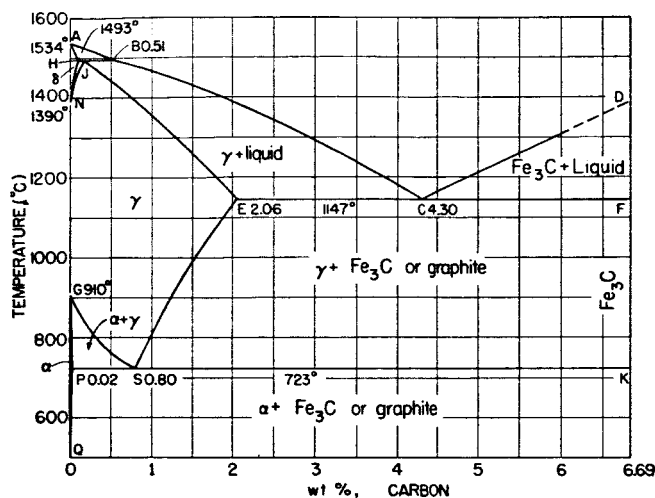


Fig. 1. Iron-carbon phase diagram (HANSEN, 1958). When a hypo-eutectoid alloy (<0.80 weight per cent C) crosses the line GS on cooling,  $\alpha$ -iron precipitates until the residual  $\gamma$ -phase has reached eutectoid composition (point S). Only then, at 723°C, does  $\text{Fe}_3\text{C}$  appear. Although  $\text{Fe}_3\text{C}$  is metastable relative to graphite everywhere in this diagram, it is favored on kinetic grounds.

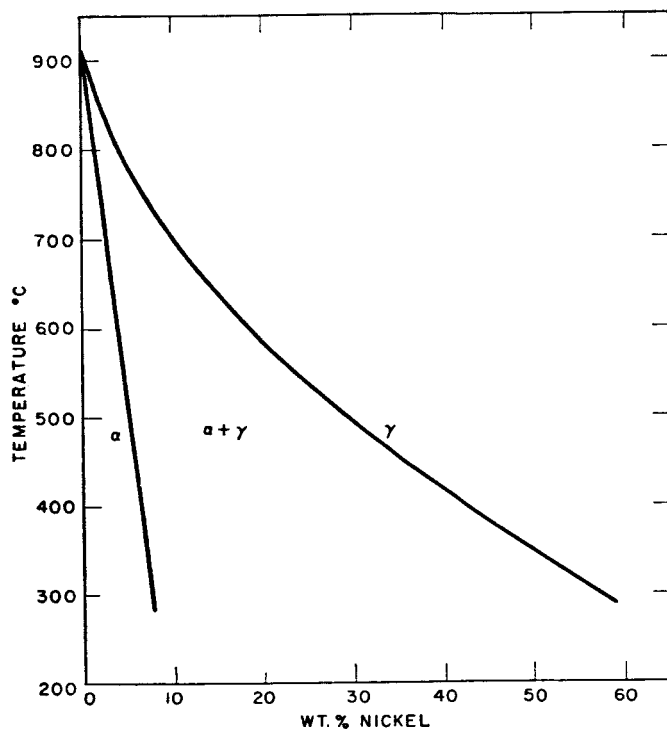


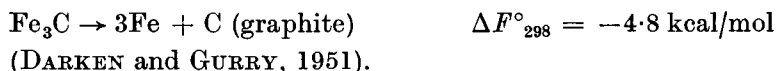
Fig. 2. Iron-nickel phase diagram (OWEN and LIU, 1949). An alloy of 7.5 per cent Ni remains homogeneous taenite down to 740°C, where kamacite first appears. On further cooling, carbon remains in the taenite until its solubility limit is reached. At this point,  $\text{Fe}_3\text{C}$  precipitates.

the  $\gamma$ -phase (taenite), while carbon- and nickel-poor  $\alpha$ -phase (kamacite) precipitates. But there is no longer a eutectoid temperature at which taenite breaks down into kamacite and cohenite. Even below 723°C, carbon-rich taenite persists, stabilised by its nickel content. As the kamacite grows at the expense of taenite, nickel and carbon concentrate in the taenite, until the alloy becomes saturated with carbon. At this temperature, well below 723°C, cohenite makes its first appearance: cohenite crystals nucleate at the kamacite-taenite interface, and continue to grow while more and more carbon is being rejected by the shrinking taenite lamellae. This continued slow growth over a substantial temperature range permits cohenite crystals in Fe-Ni-C alloys to grow much larger than the microscopic carbide particles in pearlite, the  $\text{Fe}_3\text{C}/\alpha\text{-Fe}$  eutectoid, which precipitates in Fe-C alloys on a very much shorter time scale and at a far higher degree of supersaturation. RINGWOOD (1960), on the other hand, has invoked metastability to account for this size difference.

The actual temperature at which cohenite first appeared can be estimated from BRETNALL and AXON's (1962) data. They reheated cohenite-bearing samples of Canyon Diablo at atmospheric pressure, and found that cohenite crystals redissolved completely in their kamacite matrix at 700°C in 7 days, but remained unchanged, except for a thin ferrite halo, at 650°C. These experiments do not quite duplicate the formation conditions of cohenite, since the cohenite is now in contact with kamacite of 7 per cent Ni, rather than with the original taenite of perhaps 8-11 per cent Ni. Nevertheless, the error thus introduced is negligible for our purposes, and we can conclude, for Canyon Diablo at least, that the formation temperature of cohenite (at 1 atm) lies between 650 and 700°C, most probably near 680°C. Although this figure is uncertain by perhaps  $\pm 20^\circ\text{C}$ , the conclusions reached in this paper are quite insensitive to an error of this magnitude.

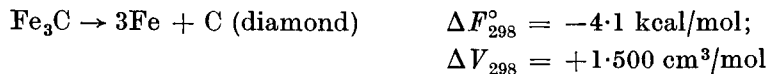
## 2. STABILITY FIELD OF COHENITE

Next, we must review the thermodynamics of the decomposition of cementite, in order to determine its formation temperature and stability field at high pressures. As pointed out above, cementite is thermodynamically unstable at low temperatures and pressures:



But this reaction proceeds with a large, positive volume change ( $\Delta V_{298}^\circ = +3.419 \text{ cm}^3/\text{mol}$ ). RINGWOOD (1960) therefore pointed out that the negative free energy would be cancelled by the  $P \Delta V$  term at sufficiently high pressures, and that cohenite would thus be stabilised by pressure.

However, we have emphasised in several of our papers (LIPSCHUTZ and ANDERS, 1961a, b) that diamond, rather than graphite will be the stable reaction product at pressures above the diamond-graphite transformation line. Consequently, the following reaction must also be considered:



If the pressures needed to stabilize cementite are calculated for both reactions, the phase diagram shown in Fig. 3 results.\* From this diagram it is seen that if iron meteorites had cooled isobarically at 30–60 kb (RINGWOOD, 1960, 1961; RINGWOOD and KAUFMAN, 1962), cohenite should have decomposed to diamond and kamacite at temperatures of 420–290°C. Its survival thus is a paradox, no matter whether the meteorites are assumed to have cooled at high or at low

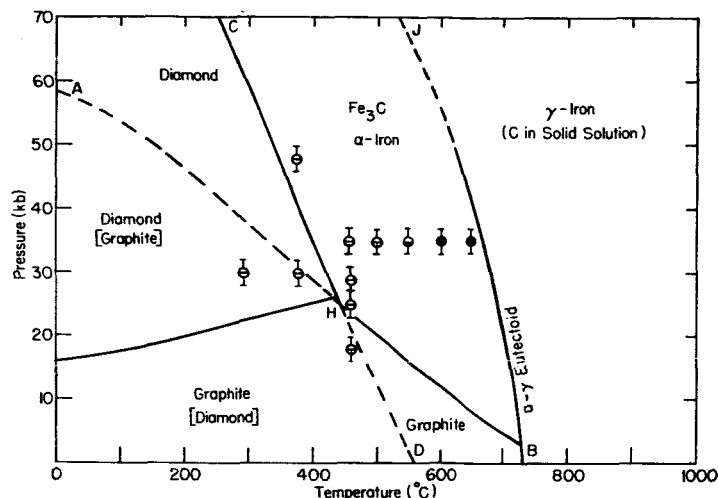


Fig. 3. Phase diagram for iron-carbon system (0.8 weight per cent C). Adapted from LIPSCHUTZ and ANDERS (1961a), but with DARKEN and GURRY's (1951) thermodynamic data for  $\text{Fe}_3\text{C}$  substituted for the original values. The  $\alpha$ - $\gamma$  eutectoid line has been taken from CLAUSSEN (1963). Metastable phases resulting from the decomposition of  $\text{Fe}_3\text{C}$  are enclosed in brackets. Cementite is stable only in the field CHBJ, but can form as a metastable phase everywhere to the left of the  $\gamma$ -iron field.

The points represent experimental measurements on the decomposition of  $\text{Fe}_3\text{C}$  (LIPSCHUTZ and ANDERS, 1961b). Filled circles: extensive graphitisation; half-filled circles: partial graphitisation; circles with horizontal bars: amorphous carbon recovered after dissolving sample in acid, but this carbon may have formed during dissolution rather than during heat treatment (see text). Decomposition of cementite in the middle of its apparent stability field shows that the true stability field of cementite must be smaller than that indicated in this diagram.

pressures. To explain this survival, it is necessary to assume that the reaction rate was very slow at these temperatures. This is an important point to which we shall return later on.

However, the decomposition of cementite at high pressures has been studied experimentally (LIPSCHUTZ and ANDERS, 1961b), and the results do not show the stabilisation predicted by RINGWOOD on the basis of DARKEN and GURRY's data.

\* In this diagram we have used Ringwood's choice of thermodynamic data ( $\Delta F_{298}^\circ = -4.76$  kcal/mol, DARKEN and GURRY, 1951), instead of the value from NBS Circular 500 ( $\Delta F_{298}^\circ = -3.5$  kcal/mol) used in our earlier paper. This change shifts the intercept of lines AB and CB with the abscissa to higher temperatures, but leaves their slopes virtually unchanged. The  $\gamma$ - $\alpha$  eutectoid temperature at high pressures was taken from CLAUSSEN's (1963) paper.

At temperatures of 550–650°C and pressures of 35 kb, deep within its calculated stability field, cementite decomposed to crystalline graphite in a matter of days (Fig. 3).\*

Clearly, the stability field of  $\text{Fe}_3\text{C}$  is much smaller than indicated by DARKEN and GURRY's data. To bring this diagram into accord with the experimental data, it is necessary to shift lines  $AB$  and  $CD$  to the right, by an amount corresponding to an error of about 2.3 kcal/mol in the standard enthalpy (Fig. 4). Such an error

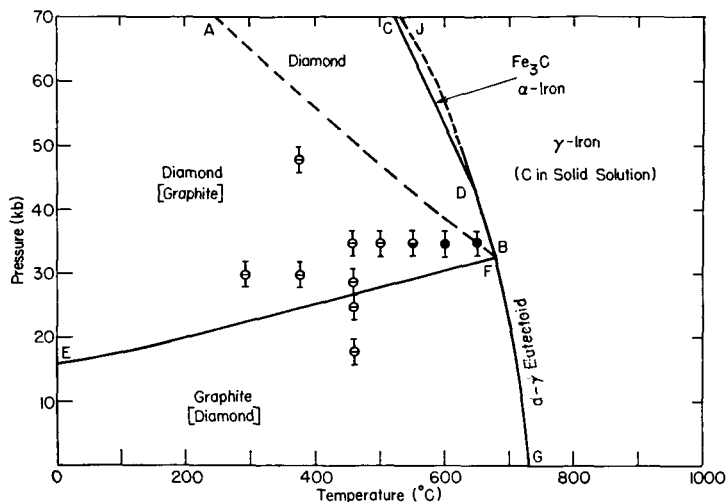


Fig. 4. Revised phase diagram for iron-carbon system ( $\leq 0.8$  weight per cent C). As in Fig. 3, with lines  $AB$  and  $CD$  shifted to the right in order to account for the observed instability of  $\text{Fe}_3\text{C}$  at high pressures. The stability field of cementite has now contracted to the region  $CJD$ .

is entirely consistent with the uncertainty in DARKEN and GURRY's extrapolation, since the data from which they derived  $\Delta H_{298}^\circ$  show several conflicting trends (Fig. 5 in their paper).

This change in the diagram may seem arbitrary, but it must be remembered that the point under discussion is the stability of  $\text{Fe}_3\text{C}$  at high pressures. Experimental data on the behavior of  $\text{Fe}_3\text{C}$  at high pressures should therefore perhaps be given greater weight than stability relations derived by indirect methods.

Now we are in a position to estimate the formation and decomposition temperature of cohenite, at any pressure. Three cases will be considered.

- (a) Cooling of iron meteorites at pressures no greater than 2.7 kb (the central pressure in Ceres, the largest asteroid). The formation temperature of cohenite will be virtually the same as at 1 atm:  $\sim 680^\circ\text{C}$ , about  $40^\circ$  below the  $\alpha\text{-Fe}/\gamma\text{-Fe}$  eutectoid temperature (Fig. 4). Since the cohenite is formed

\* At temperatures below  $550^\circ\text{C}$ , only amorphous carbon rather than crystalline graphite was found after dissolving the sample in  $\text{HCl}$ . Although control samples of cementite not subjected to heat treatment left only a minute trace of residue after  $\text{HCl}$  treatment, we are not certain that the amorphous carbon actually formed during heat treatment rather than during dissolution in acid. Perhaps the heat treatment induced some subtle changes in the cementite that favored the formation of carbon over hydrocarbons in its reaction with acid.

as a metastable phase, its decomposition temperature will also be  $680^{\circ}\text{C}$ , and the expected decomposition product, graphite.

- (b) Cooling of iron meteorites at 30 kb, the minimum pressure which RINGWOOD and KAUFMAN (1962) consider suitable for the formation of the Widmanstätten pattern. According to CLAUSSEN (1963), the  $\alpha\text{-Fe}/\gamma\text{-Fe}$  eutectoid

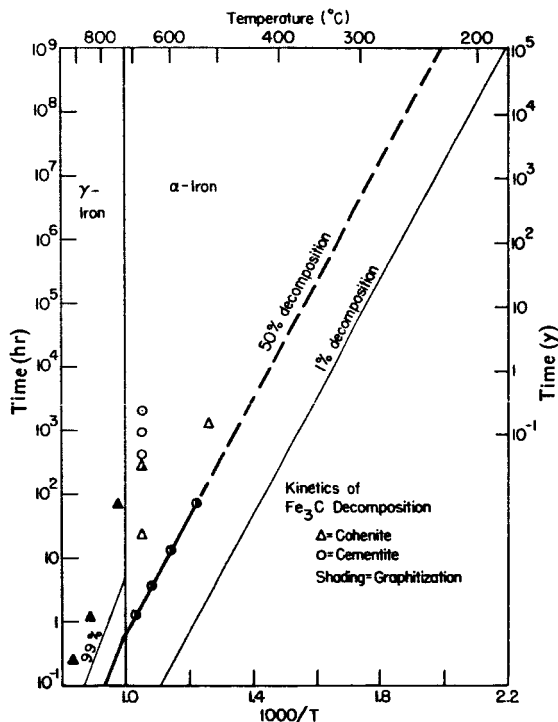


Fig. 5. Rate of decomposition of cohenite and cementite. The points through which the 50 per cent graphitisation line has been drawn are from KLEIN; the three points in the  $\gamma$ -field, from RINGWOOD and SEABROOK; and the remaining points, from this study. Cementite samples heated at  $680^{\circ}\text{C}$  for 1946 hr failed to show any graphitisation whatsoever, although similar samples with pre-formed nucleation centers show 1 per cent graphitisation in 0.03 hr. Cohenite samples decompose somewhat more readily, but the graphitisation is localised at cracks.

temperature is depressed to  $\sim 680^{\circ}\text{C}$  at this pressure (Fig. 4) and if we once again assume that cohenite formed  $40^{\circ}$  below the eutectoid, its formation temperature will be  $640^{\circ}\text{C}$ . Even at this pressure it cannot form as a stable phase. Just as in case (a), it will form as a metastable phase, and its decomposition temperature will hence equal its formation temperature,  $640^{\circ}\text{C}$ .

- (c) Cooling of iron meteorites at 60 kb, the upper limit of RINGWOOD and KAUFMAN's pressure range. Proceeding as in case (b), we can estimate the formation temperature of cohenite as  $580^{\circ}$ . It is now formed as a stable phase, however, and does not become unstable with respect to diamond until the temperature has fallen to  $565^{\circ}\text{C}$ .



It is now clear that even at the highest pressures considered by RINGWOOD, cohenite is not stabilised permanently. On further cooling, cohenite becomes unstable again, and should decompose to graphite or diamond, as shown below:

Pressure (kb)	0	30	60
Decomposition temperature (°C)	680	640	565
Decomposition product	graphite	graphite	diamond

At these temperatures the Widmanstätten pattern had not yet fully developed. Since its formation requires very slow cooling, on a time scale of millions of years, one must ask whether the survival of cohenite at these times and temperatures is consistent with laboratory data on the kinetics of cementite decomposition.

### 3. RATE OF DECOMPOSITION OF COHENITE

RINGWOOD and SEABROOK determined the decomposition time of individual cohenite crystals by heating them at temperatures of 750–950°C. Unfortunately, these results are not germane to the problem. A single cohenite crystal heated by itself represents a *hypereutectoid* alloy with 6.7 per cent C; when heated above the  $\alpha$ -Fe/ $\gamma$ -Fe eutectoid temperature, it must decompose to graphite and  $\gamma$ -iron saturated with carbon (Fig. 1). Meteorites, on the other hand, are *hypoeutectoid* alloys ( $\leq 0.8$  per cent C). As noted above, cohenite will not appear in these alloys until they cool to  $\sim 680^\circ\text{C}$ , when the taenite becomes saturated with carbon. When annealed *at or below* its formation temperature, cohenite can only decompose to  $\alpha$ -iron\* and carbon. *Above* its formation temperature, cohenite will redissolve in the surrounding kamacite as soon as the  $\alpha$ - $\gamma$  eutectoid temperature for an Fe–C alloy with 7 per cent Ni has been reached. But this situation is artificial, and has no bearing on the survival of cohenite in the meteorite parent bodies, under conditions of monotonic cooling. Hence it is essential to determine the decomposition rate of  $\text{Fe}_3\text{C}$  *below* the eutectoid temperature. A thorough study of this subject was made by KLEIN (1934). He found that in the presence of graphite nuclei, the decomposition of  $\text{Fe}_3\text{C}$  in the temperature range 550–700°C obeys first-order kinetics (with a short induction period attributed to diffusion of carbon from  $\text{Fe}_3\text{C}$  to graphite nuclei). The activation energy is 42 kcal/mol.

Figure 5 summarises the available data on the decomposition rate of  $\text{Fe}_3\text{C}$ . Two straight lines with slopes of 42 kcal/mol have been drawn to represent KLEIN's data for 50 per cent and 1 per cent graphitisation. The 50 per cent line has been extended into the  $\gamma$ -region, with an activation energy of 58 kcal/mol (KUNYAVSKIY and KHUDOKORMOV, 1960). RINGWOOD and SEABROOK's points, corresponding to "complete" graphitisation, lie somewhat above the 99 per cent line, but the disagreement is not serious in view of the uncertainty in defining complete graphitisation.

Of course, only points in the  $\alpha$ -region are pertinent to the problem. In order to provide data on the behavior of cohenite in this region, we heated cohenite-bearing

\* This is a consequence of the low Ni-content ( $\sim 2$  per cent) of cohenite. The Ni–Fe alloy formed in its decomposition will be low in Ni, and according to either Fig. 1 or 2, this alloy can exist only in the  $\alpha$ -form at or below the cohenite formation temperature.

Odessa samples and a cementite sample (a pure iron-carbon alloy corresponding to a white cast iron with 3 per cent C) to 680°C for varying lengths of time. The samples, sealed in evacuated quartz vials, were heat-treated in a furnace controlled to  $\pm 5^\circ\text{C}$ , and were quenched in cold water. They were polished and etched before and after heat treatment. Nickel diffusion is negligible at the times and temperatures involved, and the results on both cohenite and cementite can therefore be discussed in terms of the binary Fe-C diagram. According to KLEIN's data, the samples should have been 50 per cent graphitised after 1.8 hr. Actually, the cementite sample showed no decomposition whatsoever ( $\leq 1$  per cent) even after 1946 hr, while the cohenite, after heating for 355 hr, showed partial ( $\sim 10$  per cent) graphitisation, localised at cracks.

That cracks, by providing nucleation sites, accelerate graphitisation, had already been noted by BRETNALL and AXON (1962). They found that cracked cohenite lamellae in Canyon Diablo graphitised readily at 708°C in 24 hr, but that a single uncracked cohenite crystal merely dissolved in the surrounding metal, without showing any trace of graphitisation. We were able to produce the same contrasting behavior in the cementite sample, by crushing it at room temperature with a static pressure of 18,000 kg/cm<sup>2</sup>.<sup>\*</sup> During heat treatment, the crushed sample graphitised at cracks (Fig. 6), in contrast to the uncrushed sample. Cohenite, on the other hand, decomposed at cracks to about the same degree, regardless of whether the sample had been crushed or not. Presumably sufficient cracks had been produced in the cohenite during breakup of the meteorite parent body, or during impact with the earth, so that further crushing did not cause a significant increase in nucleation centers. However, there is every reason to believe that the cohenite crystals were free of cracks until the breakup of the meteorite parent body. Estimates of their decomposition rate should hence be based on uncracked material, free from shock effects.

As little as 1 per cent graphitisation would have been easily noticeable in the cementite sample heated at 680°C for 1946 hr. Actually, not a trace of graphite was found, although 1 per cent graphitisation should have taken only  $3 \times 10^{-2}$  hr, according to KLEIN. Hence the observed rate is a factor of  $> 6 \times 10^4$  slower than that expected from KLEIN's kinetic study!

But this disagreement is not entirely unexpected. As pointed out by RINGWOOD (1960), KLEIN (1934), and many others, the graphitisation of cementite requires nucleation centers: graphite particles, other impurities, or crystal imperfections. Normally such centers are produced by heating the alloy in the  $\gamma$ -region above the eutectoid temperature. If this step is omitted, graphitisation in the  $\alpha$ -region is inhibited. KLEIN remarks that white cast iron of the same composition as his samples, but without nucleation centers—"did not decompose at temperatures up to 700°C, even after heating for many days".

It is thus necessary to distinguish between two separate stages in the kinetics of cementite decomposition: nucleation and growth. In industrial alloys, the first of these is usually fast, and does not appear in the overall rate equation. But in the laboratory alloy studied by us, the nucleation rate is at least 60,000

<sup>\*</sup> This experiment was suggested by Prof. O. J. Kleppa of the University of Chicago.

times slower than the growth rate, causing the decomposition to be retarded by the same factor. We must therefore be on our guard against cases where nucleation rather than growth is the rate-determining step.

Now we can return to the central question of this paper: the survival of cohenite in meteorites. We saw above that the stability field of cohenite is quite narrow even at high pressures, and that it should decompose to diamond or graphite on cooling. We must now determine whether the rate of graphitisation is slow enough at the decomposition temperature to permit its survival.

Let us consider the three cases for which we had previously determined formation and decomposition temperatures of cohenite. The time during which cohenite finds itself at elevated temperatures and hence is in danger of decomposition, is determined by the time needed to form the Widmanstätten pattern. This time can be estimated from laboratory data, but the answers vary depending on whether high or low pressures are assumed. At low pressures, a cooling rate of  $160^{\circ}/\text{m.y.}$  seems to be required (WOOD, 1963). At higher pressures, the  $\gamma$ - $\alpha$  transformation temperature is depressed; to allow the necessary diffusion of nickel to take place, a slower cooling rate and longer time must be assumed. RINGWOOD and KAUFMAN (1962) estimate a formation time of  $10^8$  yr. This is equivalent to an average cooling rate of  $11^{\circ}\text{C}/\text{m.y.}$ , if the entire temperature drop from  $1500^{\circ}$  to  $400^{\circ}\text{C}$  is assumed to have taken place in this interval.

Once the temperature has fallen below the decomposition temperature of cohenite,  $T_d$ , the reaction will proceed continuously. Owing to the exponential decrease of the rate constant with temperature, most of the decomposition will take place near  $T_d$ . In fact, one-half the total decomposition will take place in the first half-life, defined as the time during which the temperature decrease causes the rate to drop to one-half its initial value. It follows that the total decomposition, during cooling from  $T_d$  to some final temperature where the rate becomes negligibly slow, will be exactly the same as if the sample had been held at  $T_d$  for an "effective time" equal to one mean life ( $t_{1/2}/0.693$ ). These effective times, or times available for decomposition, may be compared directly with the decomposition times predicted from laboratory experiments (Table 1). The last column gives the inhibition factor: the ratio of the available decomposition time to the time required for 1 per cent decomposition in the laboratory.

Clearly, cohenite has failed to make use of the opportunity to decompose, although the available times were  $10^{10}$ – $10^{11}$  times longer than those required for 1 per cent decomposition. This is equally true at high and at low pressures. Hence it is no longer possible to attribute the survival of cohenite to high pressures.

In making this comparison, we have tacitly assumed that the decomposition of cohenite to diamond will proceed at about the same rate as its decomposition to graphite. This assumption is probably justified. The rate-determining step in the decomposition reaction is probably not the diffusion of carbon atoms through  $\alpha$ -iron (for which the activation energy is only  $20.1$  kcal/mol: WERT, 1950), but the rearrangement of iron in the cementite lattice to the body-centered cubic structure of  $\alpha$ -iron. The activation energy for the latter process should be the same regardless of whether carbon is eliminated as graphite or diamond.

One might be tempted to rescue the high-pressure hypothesis by some special

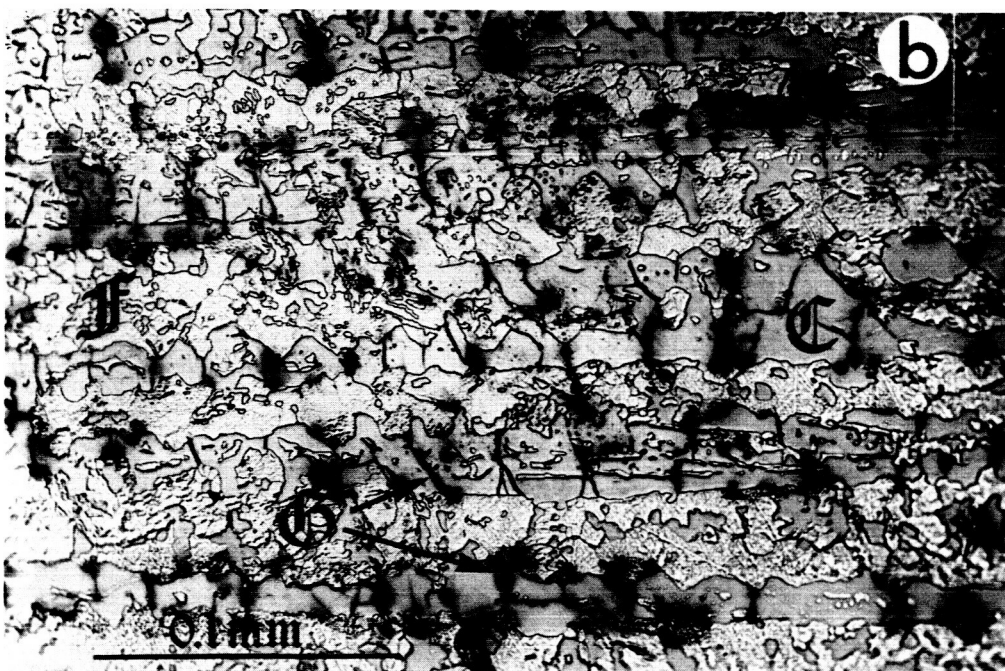
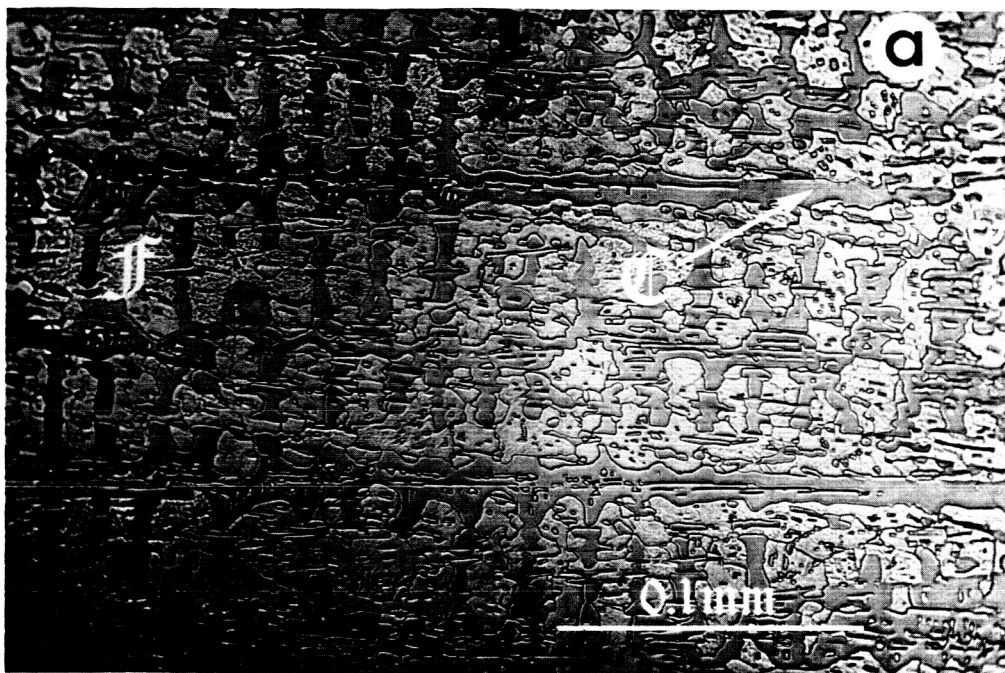


Fig. 6. Effect of crystal perfection on graphitisation rate. An untreated cementite sample (a) showed no graphitisation after 355 hr at 680 C, while an identical sample (b) crushed with a static pressure of 18,000 kg/cm<sup>2</sup> before heat treatment graphitised readily at cracks. Although the area photographed was rather more extensively cracked and graphitised than the sample as a whole, a measurable degree of graphitisation was visible throughout the specimen. C = cementite; F = ferrite ( $\alpha$ -iron); G = graphite.

assumption. Could it be that the decomposition rate of  $\text{Fe}_3\text{C}$  at high pressures is much lower than the rate at 1 atm upon which these comparisons are based? Fortunately, there exist laboratory data on this question. Cementite heated

Table 1. Comparison of cohenite decomposition rate with times available for decomposition

Pressure (kb)	Cohenite Formation temp. ( $^{\circ}\text{C}$ )	Cohenite Decomposition temp. ( $^{\circ}\text{C}$ )	Predicted time for 1% decomposition (hr)	Effective time at decomposition temp. (y)	Inhibition factor
<2.7	680 $^{\circ}$	680 $^{\circ}$	0.026	$2.4 \times 10^5$	$8.1 \times 10^{10}$
30	640 $^{\circ}$	640 $^{\circ}$	0.068	$2.9 \times 10^6$	$3.7 \times 10^{11}$
60	580 $^{\circ}$	565 $^{\circ}$	0.56	$1.5 \times 10^6$	$2.4 \times 10^{10}$

under 35 kb pressure graphitised extensively after 48 hr at 600 $^{\circ}\text{C}$  and 69 hr at 650 $^{\circ}\text{C}$  (LIPSCHUTZ and ANDERS, 1961b). The half-times for graphitisation at these temperatures, as given by KLEIN's data, are 13 hr and 3.3 hr. Hence there is no significant difference between the high-pressure and low-pressure decomposition rates in the laboratory.\*

It does not seem possible to attribute the survival of cohenite to stabilisation by trace elements. The present phosphorus content is evidently too low, and nickel, although present in greater amounts (BROWN and LIPSCHUTZ, 1963), can at best stabilise it by 0.20 cal mole $^{-1}$  deg $^{-1}$  due to the entropy of mixing.

Only one possibility seems to remain: slow nucleation. Our own experiments show that absence of nucleation centers inhibits graphitisation of cementite at 680 $^{\circ}\text{C}$  by a factor of  $>6 \times 10^4$ . Data from other authors (HICKLEY and QUARRELL, 1954) indicate factors of  $>10^5$ . In meteorites, factors of  $10^{10}$ – $10^{11}$  are needed, and while we do not expect to be able to prove experimentally within our lifetimes that such factors are realistic, we want to point out a few reasons why nucleation might be slower in meteorite parent bodies than in the laboratory.

Nucleation in commercial Fe–C alloys is usually enhanced by Si or Al; apparently, because the (1 $\bar{1}$ 00) planes of graphite nucleate readily on the (110) planes of cristobalite and  $\gamma$ -alumina (HICKLEY and QUARRELL, 1954). In support of this mechanism, these authors showed that the rate of graphitisation of Fe–C alloys containing free Si was very slow *in vacuo*, but increased with increasing partial pressure of oxygen. Cohenite-bearing iron meteorites have undoubtedly formed under an exceedingly low partial pressure of oxygen, and they do not contain cristobalite or  $\gamma$ -alumina. Any other oxides present are usually localised in troilite nodules where they are out of contact with the cohenite. Other types of nucleation centers, such as dislocations, cracks, and impurities, are likely to be much rarer in cohenite crystals grown by slow cooling during  $10^5$ – $10^7$  y than in

\* It was pointed out by a referee that the rates of decomposition of cementite observed by us at high pressures might be abnormally fast, owing to shearing stresses in the squeezer apparatus. Under true hydrostatic conditions the rate might be much slower. While this argument may be perfectly valid, it still leads to essentially the same conclusions as ours: that the survival of cohenite is due to kinetic rather than thermodynamic factors. In either case, cohenite loses its utility as a pressure indicator.

commercial alloys cooled within minutes or hours. The activation energy for graphite nucleation on cristobalite is 79 kcal/mol between 800 and 1000°C (BURKE and OWEN, 1954), but for less favorable nucleation centers the activation energy may well be considerably higher. Finally, the free energy difference between cementite and graphite is so small near its formation temperature, that it may be more than offset by the surface energy, which will favor millimeter-sized cohenite crystals over Angström-sized graphite nuclei. To sum up the matter: if relatively imperfect cementite crystals heat-treated in the laboratory show inhibition by factors of  $>10^5$ , is it entirely unreasonable to suppose that the larger and much more perfect meteoritic cohenite crystals were inhibited by factors of  $10^{10}$ – $10^{11}$ ?

RINGWOOD (1960) has argued that iron meteorites, having cooled slowly through the temperature range 1000–700°C where “graphite nuclei are readily and quickly formed”, should provide a very favorable medium for the decomposition of cohenite. Actually, the opposite is more likely to be true. *Hypoeutectoid* alloys will not form graphite nuclei, since they can retain all their carbon in solution down to 680°C, where cohenite first forms. *Hypereutectoid* alloys, on the other hand, will precipitate graphite at temperatures above the eutectoid, but since carbon can diffuse freely at the enormously long cooling times available, this graphite will segregate at the periphery of troilite nodules, rather than remaining dispersed in the metal, where it might later provide nucleation centers for the decomposition of cohenite. This is in accord with observation: graphite is never found in the metal but only in and around nodules of other minor constituents.

We admit that the notion of reaction inhibition by a factor of  $10^{11}$  grossly violates one of the most basic premises in geology and meteoritics: that times were long enough for equilibrium to be reached. Every effort should therefore be made to find alternative explanations of the survival of cohenite. However, one point may already be stated with emphasis: *cohenite initially stabilised by high pressures becomes unstable again on cooling, and cannot survive, unless its decomposition is inhibited by a factor of  $10^{11}$* . Since inhibition by the same factor is required at low pressures, there is no longer any reason to regard cohenite as a “pressure indicator” in iron meteorites.

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